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MARCASITE FROM THE UPPER MISSISSIPPI VALLEY ZINC  
AREA AS A SOURCE OF SULPHUR

BY

CARL ROBERT CHRISTIANSEN

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A

THESIS

submitted to the faculty of the  
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF  
MISSOURI

in partial fulfillment of the work required for the

Degree of

ENGINEER OF MINES

Rolla, Missouri

1952

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Approved by -

*J. S. Forester*

Professor of Mining Engineering

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## INTRODUCTION

Sulphur is a mineral material which is as basic as steel to our industry and economy. This fact is not generally realized because it is seldom seen, but it goes into the manufacture of practically every article of clothing we wear, and the food we eat is dependent upon it. Most items we produce require the use of sulphur at some stage of their manufacture. The consumption of sulphur has been increasing rapidly and is now far above its World War II peak. Production has been greatly increased but has been unable to keep up with the increasing demand. This situation is extremely critical because the world reserves of natural sulphur are being rapidly depleted.

In the United States, the consumption of sulphur has increased from 1,500,000 tons in 1939 to an estimated 5,350,000 tons in 1950.<sup>(1)</sup> At this same rate, consumption will have increased to 9,000,000 tons annually in another decade. Experts estimate that, at the 1950 rate, there is only about a ten-year supply left.<sup>(2)</sup> Obviously, the need for sulphur is most urgent and other sources of supply must be brought into production.

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(1) Williams, L.M. Jr., The Crisis in Sulphur, Freeport Sulphur Company, 1951, p.16.

(2) Sulphur Short World, The Northern Miner, p.4, Apr. 12, 1951.

The principal world sources of sulphur are:

- 1) native sulphur or brimstone--deposits of S in its "free" or elemental form.
- 2) pyrites--iron sulphide ores containing 40 to 53 per cent S.
- 3) natural gas--containing S in the form of hydrogen sulphide.
- 4) petroleum refinery gas--containing hydrogen sulphide.
- 5) smelter gas--which contains S as sulphur dioxide.
- 6) gypsum--a mineral which contains about 20 per cent S as calcium sulphate.
- 7) coal--containing S as pyrites (coal "brasses") and organic compounds.

Almost every nation has sulphur in some form, so one might wonder as to the reason for a shortage. It is wholly a matter of economics. Four-fifths of all sulphur is used to make sulphuric acid<sup>(3)</sup>, which can be produced from any form of sulphur. Before World War II, the nations that now make up the Free World got most of their sulphur--not from American brimstone, our principal form--but from other sources, primarily pyrites. Pyrites was produced in 21 of these countries, native sulphur in 11, and other forms of sulphur in 13. After World War II, foreign acid makers, in rebuilding

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(3) Williams, op. cit., p.10.

war damaged plants or in constructing new plants, turned from their traditional sulphur sources to American brimstone for economic reasons. Acid plants using brimstone cost far less in money and time to build and operate (an acid plant designed to burn pyrites costs about 1.75 times that for a plant burning brimstone and operating costs are about 1.7 times those for a plant burning brimstone<sup>(4)</sup>), and more importantly, American brimstone is the cheapest and purest of all the various forms of sulphur. As a result, the rest of the world has become dependent on U. S. brimstone to supply a greater share of its needs than was the case before the war.

The increased demand from foreign countries plus the enormous increase in domestic consumption have made it necessary for our sulphur producers to bring their production to a record high, but even these efforts have been inadequate to meet the demand. The production of brimstone would supply all of our domestic needs, but we must also supply other countries with sulphur to enable them to maintain industrial production and strengthen their economic situation. For this reason our government is directing American brimstone producers to ship large tonnages of brimstone overseas. Exports in 1951

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(4) Sullivan, J.D., and Swager, W.L., Sulphur, Mining Engineering, Vol. 3, No. 5, pp. 403-409, May 1951.

(5)  
will be approximately 1,300,000 tons of sulphur .

Our industries must get along on what is left and as a consequence the use of sulphur in the United States has been rationed, as there is not enough to meet all of our needs.

The United States government has imposed economic controls to prevent increased costs and inflation. These controls have prevented sulphur prices from rising as would normally happen when a shortage occurs. A higher price for sulphur would tend to bring out more production from higher-cost sources. Despite vast exploration programs, no extensive new brimstone deposits have been found, so production cannot be increased further. The increased demands of industry must, therefore, be supplied from the higher-cost sources. The world, as a whole, is not getting this additional sulphur because the price of American brimstone is so low that it discourages production from these other sources. Thus, the rest of the world relies upon America's resources. It is essential that these other sources of sulphur be developed rapidly; for our stockpiles of mined sulphur must not be reduced beyond their present level, which is at a minimum for national security. These stocks have declined from a pre-war peak of two years' supply to the

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(5) Williams, op. cit., p.20.

present low of a quantity of sulphur which would supply our needs for only six months.

Many other sources of sulphur are now being investigated to provide supplements to the present production. Iron sulphides in the form of pyrite, pyrrhotite, and marcasite have been used as a source of sulphuric acid, and are now receiving more attention in the United States and Canada. Low grade elemental sulphur deposits in the western U. S. and in South America have been studied and a recovery method devised, so these promise to provide an important additional supply of brimstone. The author of this paper has investigated the possibilities of the Upper Mississippi Valley zinc and lead district as a potential producing region of iron sulphide concentrates which might be used in production of sulphur compounds to acid in satisfying the demands of the surrounding industrial area.

Iron sulphide, chiefly in the form of marcasite,  $\text{FeS}_2$ , is associated with the zinc and lead ores of southwestern Wisconsin, northwestern Illinois and eastern Iowa. Assays of the local ores reveal the presence of from 5 to 12 per cent iron, with which would be combined a slightly higher percentage of sulphur to form iron sulphide. Daily production of mine-run ore from the district now totals approximately 4200 tons and promises to be substantially increased due to activity in development of new properties and expansion of existing facilities.

From this volume of ore, sufficient sulphuric acid could be obtained to be of great aid to industries of the region.

Pulp and paper companies are the immediate, large potential consumers of iron sulphide and the current sulphur shortage is causing them to give serious consideration to switching over to the use of iron sulphide rather than brimstone. Pyrite or marcasite can be employed equally as well as brimstone in the manufacture of sulphite pulp, used in making the best grades of paper; but brimstone has been inexpensive, is easy to work with, and there is the capital cost of the additional burning plant for pyrite to be considered. About 275 pounds of sulphur goes into the manufacture of a ton of the sulphite papers. Most of the pulp-paper companies burn brimstone to form sulphur dioxide gas. This gas is dissolved in water to make sulphurous acid, which is needed for the sulphite pulp. Pyrite also can be burned to form sulphur dioxide; but, it requires a different type of burning equipment. New equipment would have to be installed at considerable expense; but the pulp producers would be willing to go to this expense to insure continued paper production. However, before making this conversion, they want to be assured that a continuous and adequate supply of pyrites would be available at a fair price. The paper mills face a 15 to 20 per cent

reduction in the sulphur allotted to them and this would mean a corresponding cut in their paper production.

This makes the iron sulphide of the Upper Mississippi Valley very attractive to the tremendous pulp-paper industry of Wisconsin and the adjacent states.

In addition to the paper industry, many other industries in the surrounding area are extremely interested in the possibility of obtaining sulphuric acid from this district. The Algonquin Chemical Company, which burns sulphur in Dubuque, Iowa; only 20 miles from the largest mines in the district provides a potential market for iron sulphide concentrates and has shown interest in the project.

The Dorr Company, Engineers, of Stamford, Connecticut have devised a new method of producing sulphur dioxide gas from sulphide ores<sup>(6)</sup>. This is called the FluoSolids System. The equipment is simple and compact, and should prove entirely satisfactory for acid production or for paper mill use with the local iron sulphide concentrates.

With a market for the product and satisfactory roasting equipment available the problem that remains is to produce a high grade iron sulphide concentrate;

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(6) The Dorr Company, Bulletin No. 7500.



and to produce it at a price that will make it profitable to both the prospective purchaser and to the mine operator. The latter portion of the problem involves a number of economic variables which will be partially covered in calculations near the end of this report. The main part of this investigation was concerned with the production of the concentrate of sufficiently high grade and at the same time to secure good recovery. The problem presented difficulties which are not found in the concentration of pyrite or pyrrhotite. The local marcasite usually is very dull, lacking the bright metallic luster of pyrite; and it tends to oxidize rapidly on the surface, making it much more difficult to recover by flotation than pyrite. It's brittleness causes it to crush to extremely fine particles in the normal crushing and grinding operations. The presence in the ore of an oil-bearing shale which floats and slimes easily causes further complication by tending to oppose separation.

In the years before World War II, part of the iron sulphide from the local ores was used in the manufacture of sulphuric acid. The Vinegar Hill Zinc Company operated a custom mill at Cuba City, Wisconsin, and obtained lead and zinc concentrates which were shipped to smelters in Illinois. The tails from the zinc flotation circuit were sent to an iron flotation circuit where an iron

sulphide concentrate was produced. This concentrate was roasted in a Wedge furnace in the acid plant on the property. However, this iron sulphide concentrate averaged only 37 per cent sulphur due to the aforementioned difficulties, and this grade is too low for commercial use. Prospective purchasers want a minimum of 45 per cent sulphur in the concentrates, thus it was necessary to revise the concentration process to produce a marketable material.

In conjunction with the mining companies producing ore in this district, research was conducted in the ore dressing laboratory at the Wisconsin Institute of Technology to find a satisfactory concentration process.

## REVIEW OF LITERATURE

Of much interest to the mineral industries is the new process for the refining of low grade sulphur ores announced by the Chemical Construction Company, subsidiary of American Cyanamid Company. Chemico says that they can process any deposit having more than 30 per cent free sulphur content and produce a 99.5 per cent pure sulphur product for between \$15 and \$18 a ton, net cost at the mine. Surveys indicate that there are large deposits of this low-grade material which may be mined from the surface throughout the world. Many millions of tons of sulphur in this form may be found in California, Wyoming, and other western states; and a vein running through the Andes of South America is estimated to contain at least another 100 million tons. A description of the process which presents an economic method of refining this material is given in the Chemical and Engineering News, Volume 29, No. 7, February 12, 1951, page 560.

In Canada, Noranda Mines has developed a process to make full use of pyrite, and plans to spend four million dollars on a plant to treat it <sup>(7)</sup>. The biggest feature of the Noranda process is that it will produce elemental sulphur from pyrite. The first plant will have

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(7) Sulphur Short World, Northern Miner, April 12, 1951, p.4.

a daily capacity of 300 tons of pyrite. This quantity of pyrite will have a sulphur content of 150 tons, of which 40 per cent or 60 tons will be recovered as elemental sulphur. Additional sulphur will be recovered in the form of sulphur dioxide which will be used in sulphuric acid plants. A high grade iron residue, amounting to about 100 tons per day, will be available for sale to steel plants. The Noranda process is patented and has secret details, but a general description may be found in the April 12, 1951 issue of the North-ern Miner.

Very little has been written about iron sulphide recovery, probably due to its past lack of importance. In most mining operations it is considered a gangue mineral and goes to waste. Lack of acid plants burning sulphur have made it useless to attempt to recover it; and long distances to other markets, combined with the very low market price, made it economically impossible to attempt commercial recovery in most mining districts. Bright pyrite is usually easily concentrated into a high grade product; but in the Wisconsin-Illinois district, where iron sulphide is found and could have a market, it is found in the form of the more difficult to concentrate mineral, marcasite. Therefore, the literature on pyrite concentration can be used only as a rough guide. The standard references on ore dressing,

such as Taggart's Mineral Dressing, the literature published by the American Cyanamid Company and Denver Equipment Company were used as guides in selecting processes, reagents, and equipment.

## DISCUSSION

The ores of the Wisconsin-Illinois district consist of zinc, lead, and iron sulphides in a country rock of magnesian limestone; and, in most mines, an oil shale is associated with the ores. The ores of the district will assay: 0.25 to 1 per cent Pb, 3 to 8 per cent Zn, and 5 to 12 per cent Fe. At the present time, no attempt is made at any of the concentrating mills to recover the iron sulphides.

The mills of this district have basically the same methods of concentration. The ore is crushed, then jigged to eliminate part of the lighter components. The jig concentrate goes to the grinding circuit, then to the lead flotation cells. After removal of the lead sulphide, the material goes to the zinc flotation cells which produce the zinc concentrate and tailings. The tailings contain the iron sulphides along with dolomite and some oil rock; and this product is run into tailings ponds.

The tests that were made by the author to determine the best method of recovery of the iron sulphide made use of ores from the Vinegar Hill Zinc Company mines and the Calumet and Hecla mine, both in the Shullsburg, Wisconsin area. As the ores from all mines in the district are of the same type, the problem of sulphur recovery would be much the same in each case. Ores from several

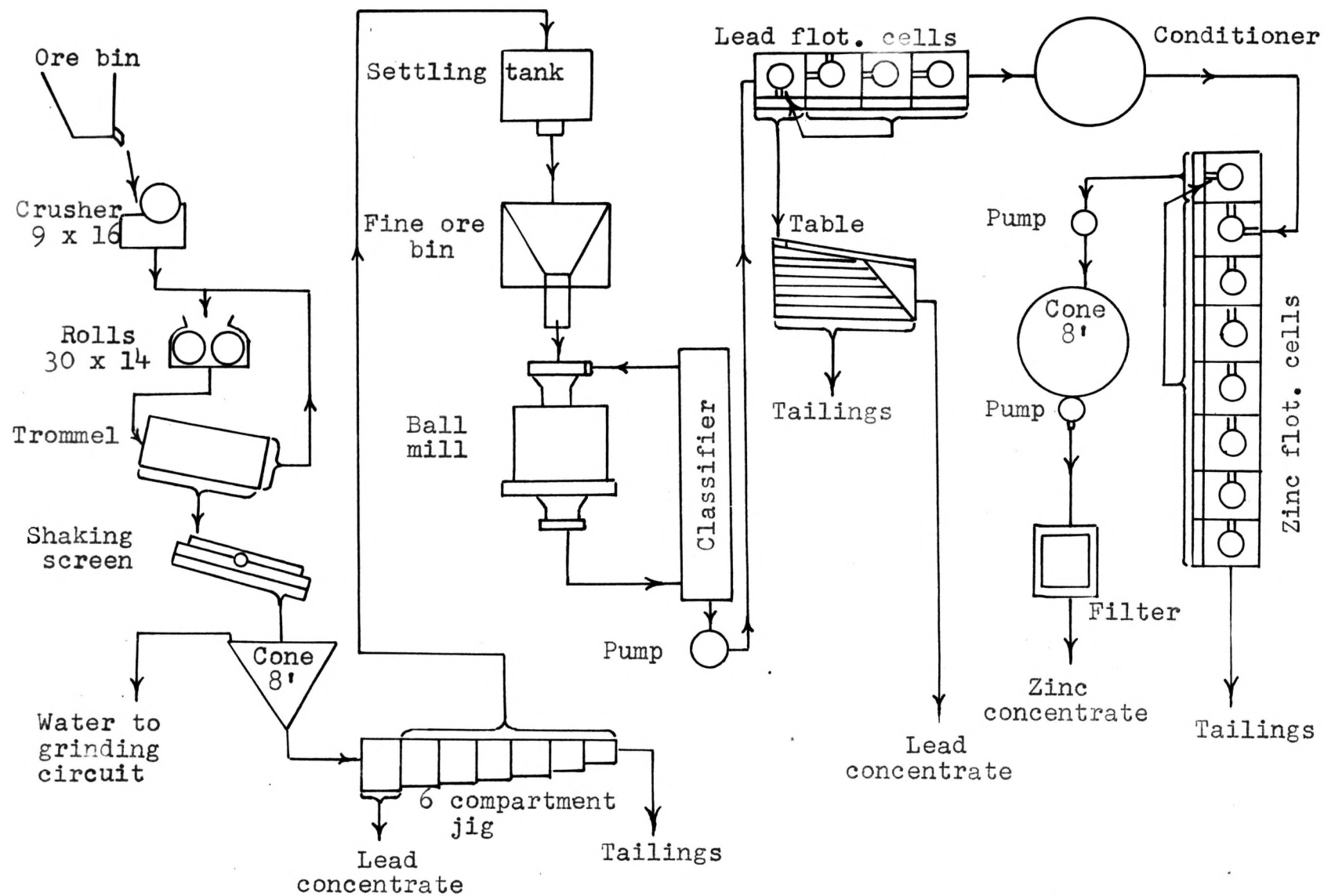


Figure 1. Flowsheet of 200 ton mill typical of the district.

mines were tested, but to insure proper correlation of experimental data, only the results of tests on Vinegar Hill Zinc Company ore will be shown in this report.

The objectives to be sought for in the recovery process were discussed by the author with local mining company officials, members of the Institute of Technology mining department, and prospective buyers of  $\text{FeS}_2$  concentrate. These objectives are listed below:

- 1) The concentrate must contain a minimum of 45 per cent sulphur in the form of iron sulphide. This is considered to be the lowest permissible grade by prospective purchasers for burning; and as transportation charges are a major item, waste material must be kept at a minimum.
- 2) The process must not require any important changes in the present mill flow sheet for lead and zinc.

It is not expected that sulphur recovery will result in high profits, and as the market for sulphur in this form may be short lived, the present satisfactory milling methods for lead and zinc should not require major revision.

- 3) The cost of the additional equipment and plant construction must be kept to a minimum.

To avoid loss in case of mine shutdowns due to low metal prices, or because of the availability of a cheaper source of sulphur, the operators do not



want to purchase large amounts of expensive equipment, or to construct new mill buildings.

- 4) A sulphur recovery of 90 per cent is desired in the concentration process.
- 5) The moisture content of the iron sulphide concentrate must be kept as low as possible.

Excess water is undesirable in the burning of the sulphide ore; and to the shipper it is costly, for he must pay freight on water. To make the enterprise profitable, the transportation charges will have to be kept down.

- 6) The amounts of certain elements in the  $\text{FeS}_2$  concentrate must be kept below maximums as given by prospective purchasers. Lead and zinc shall be less than 1 per cent. Arsenic and selenium are also undesirable.
- 7) For the FluoSolid System of roasting, the  $\text{FeS}_2$  concentrate should be smaller than 20 mesh.

#### Selection of Method of Recovery

An examination of the objectives listed above led to the conclusion that the recovery of iron sulphide should be made from the tailings from the zinc flotation cells. Any attempt to make the separation at another point in the circuit would necessitate changes in the present flow sheets of the lead-zinc mills, and this would mean more expense, shutdown for alterations, and

revision of mills that are considered satisfactory for their purpose. As the mills are now operating, the tailings from the zinc cells go directly to the tailings pond; thus, any installation made to concentrate the iron sulphide at this point would cause no interference with the present operations. Equipment could be installed, necessary construction done, and the new machinery put into operation without requiring shutdown or any alteration of the existing processes.

Various types of concentrating devices were considered with the previously stated objectives in mind. These requirements seemed to eliminate all but two types of equipment. The Humphrey's Spiral Concentrator seemed well suited in most ways. The apparatus is simple; power, reagent, labor, and maintenance costs are low; and the installation is compact, requiring little additional space, so construction costs would be low. The other possibility was flotation, which had been used before by the Vinegar Hill Zinc Company, but with poor results, as the concentrate was of too low grade to satisfy present requirements.

Before attempting any tests with either type of equipment a complete screen analysis was made of the tailings from the zinc flotation circuit. This analysis is shown in Table 1.

A study of this table will reveal the grinding characteristics of the marcasite. In this sample 70

<u>Mesh Size</u>	<u>% Wt.</u>	<u>Cum. % Wt.</u>	<u>% Fe.</u>	<u>Wt. x % Fe.</u>	<u>% Fe Dist.</u>
+20	0.00	-	-	-	-
+28	0.03	0.03	2.00	0.6	0.01
+35	0.14	0.17	2.50	3.0	0.03
+48	0.72	0.89	2.60	16.1	0.15
+65	2.99	3.88	3.20	82.9	0.75
+100	7.92	11.80	6.30	432.2	3.94
+150	8.70	20.50	10.50	791.7	7.22
+200	9.52	30.02	14.80	1221.0	11.14
+325	14.87	44.89	16.00	2062.4	18.82
-325	55.11	-	13.30	6350.7	57.94
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
Totals	100.00	100.00	(12.65)	10960.6	100.00

TABLE I  
Screen Analysis of Vinegar Hill Zinc Mill Tailings

per cent of the material is minus 200 mesh in size and 80 per cent of the iron is found in the size range. While almost 4 per cent of the tailings is plus 65 mesh, less than 1 per cent of the iron is found in this coarsely ground portion. Because the marcasite is ground to such a small size, some difficulty in concentration is apparent. The grind in the sample of Table no. 1 is finer, undoubtedly, than it should be, due to an underloaded ball mill; however, it serves to show the size distribution; and additional screen analyses with a coarser grind showed that most of the iron sulphide still was found in the minus 200 mesh size.

The Humphrey's Spiral Concentrator manufactured by the Colorado Iron Works operates successfully on sizes between 35 and 200 mesh. As the marcasite is largely found in the minus 200 mesh and even minus 325 mesh sizes, it is out of the proper size range. Even with a coarser grind, the marcasite sizing is still out of this range. As a consequence of this analysis, the Humphrey's Spiral was eliminated as a possibility in the concentration of the iron sulphide in the zinc tailings; and flotation was chosen for the job.

The experimental work for the concentration of marcasite from zinc tailings was done in the laboratories of the Wisconsin Institute of Technology. The flotation equipment used consisted of the following: two 800 gram Fagergren type laboratory flotation machines (batch type),

and a 2000 gram Fahrenwald batch type machine. Buechner filtration apparatus was used to determine the filtering characteristics of the concentrate.

The objective of the experiments was to find a simple, low-cost procedure which would give a high-grade concentrate with high recovery. Articles on flotation reagents and procedure were used as references. The plan to be followed in the experimental runs was as follows: first, select the per cent of solids in the flotation feed which seems to give best results; second, to determine the flotation time required in the rougher cells to give satisfactory recovery; and then after determining this basic information by using standard reagents and procedure the per cent solids and flotation time required would serve as a basis for the experiments to follow. Variations would be made on all of the other factors that enter into the results of concentration by flotation.

The tailings from the zinc flotation circuit of the Vinegar Hill Zinc Company, which were used as heads for the  $\text{FeS}_2$  circuit averaged 23 per cent solids, had a pulp density of 3.3, and a pH of 8.3 .

The preliminary tests to determine the pulp density and flotation time to be used in the subsequent tests made use of the following procedure. Isopropyl xanthate was used as the promoter in the amount of 0.2 pounds

per ton of feed, and pine oil was used as the frother. The xanthate was added to the feed, conditioned 3 minutes, followed by addition of the pine oil and another minute of conditioning before flotation was started. Several tests were run while the frothing action was watched, and the froth and tails visually analyzed with the aid of a vanning placque. In addition to the visual examination, chemical analyses were made of the concentrate and tails produced. The first analyses showed that 20 to 25 per cent solids in the head feed would be most satisfactory. This percentage not only gave as good recovery and grade as any other; but it also has another definite advantage. No thickener would have to be installed to remove excess water from the zinc tails before they are fed to the iron circuit, because the zinc tails average 23 per cent solids. This figure is also preferable to a smaller per cent of solids, for flotation machine capacity is usually proportional to pulp density<sup>(8)</sup>; thus the use of a low pulp density would necessitate additional flotation cells and would increase the cost of the installation needed. A high pulp density also would be undesirable for this material because of the extremely fine grind and slime content.

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(8) Gisler, H. J., *Factors Affecting Flotation*, Deco Trefoil, Vol. 15, pp. 9-10, Aug. 1951.

Experience in most districts has proved that the ratio<sup>(9)</sup> of sand to slime in a pulp limits the optimum density. Thus, a flotation feed consisting of 20 to 25 per cent solids provides an average which will give the best recovery at the lowest cost.

The time required to produce the rougher concentrate was determined to be eight minutes. At the end of a six minute period the froth was almost free of iron sulphide particles, but an additional two minutes was allowed to insure good recovery and as a factor of safety to allow for the possibility of some increase in production after the installation of equipment. Increasing the roughing time beyond eight minutes did not noticeably improve the recovery and increased the amount of waste material added to the rougher concentrate.

The results of these preliminary tests indicated that the remainder of the experiments should be carried on with two constants: approximately 23 per cent solids, and 8 minutes of rougher cell time. The other factors entering into the success of concentration are: (a) pH value of the feed, (b) size of grinding, and (c) the chemical reagents to be used.

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(9) Ibid.

## SELECTION OF REAGENTS

A complete variety of flotation reagents was provided by the American Cyanamid Company, and the next step in the problem was the selection of a satisfactory combination of the reagents. The Vinegar Hill Zinc Company mill makes use of pine oil as the frother in the zinc flotation circuit so it was decided to continue its use in the iron circuit as a starting point, and to experiment with others in following tests.

All available promoters were examined to determine their suitability for flotation of iron sulphide in a carbonaceous gangue, and preferably in an alkaline circuit. The Aerofloat reagents were eliminated as they are not effective promoters of iron sulphides in alkaline circuits. Usually it is desirable to float in an alkaline or neutral circuit <sup>(10)</sup>. Low pH or acid circuits usually require specially constructed equipment to withstand the corrosive action of the pulp, and it is often difficult to counteract this condition due to soluble salts which form by reaction of the ore with the acid reagent. American Cyanamids 400 series reagents were eliminated for they are good promoters of oxidized sulphide ores; and iron in oxide form had to be depressed to produce a high sulphur content in the concentrate.

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(10) Ibid.



The 300 series--Xanthates, seemed to meet the general requirements of the promoter needed here. They are strong promoters, effective for bulk flotation of sulphide ores<sup>(11)</sup>. These were used in complete flotation tests with good success. The effect of these reagents can be seen by referring to the tables of metallurgical results. The amount of oxide iron in the flotation concentrate indicates that these did not promote enough of these oxides to cause serious reduction in the percentage of sulphur in the concentrates.

Although a concentrate of good grade was obtained, it was felt that it might be improved if more of the carbonaceous slimes and oil rock could be eliminated. Two of American Cyanamids 600 series depressants were tested to determine their effect. Both 610 and 645 raised the grade of the concentrate very slightly but they offset this fact by a small decrease in recovery, so it seems doubtful that they will be of sufficient value to justify their use.

The pH of the tailings from the zinc circuit averages 8.3 to 8.5. On the assumption that iron sulphide might float more satisfactorily in a less alkaline condition, the pH was reduced in the iron circuit after a successful combination of the preceding factors was

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(11) Mineral Dressing Notes, No. 15, p. 7, Jan. 1947.

selected. The results of reducing the pH by addition of sulphuric acid were not better than at 8.3; thus the elimination of the need of the scarce sulphuric acid with its detrimental effect on equipment was shown to be possible.

The next factor to be varied was the size of the feed to learn of its effect on grade and recovery. As a general rule an ore should be ground only fine enough to unlock the values<sup>(12)</sup>, and the most efficient mineral dressing process will result. Screen analyses were made of the flotation feed and compared with the resultant recovery and grade. Graphs showing the relationship between these results and the size of grind are shown on pages 36 and 37.

Most of the tests were made by producing a rougher concentrate which was then put through a cleaner cell. A cleaning time of 2 minutes proved adequate to give the required grade of concentrate and adequate recovery. Best results in cleaner cells are obtained with a dilute pulp, and about 5 per cent solids proved satisfactory in this case. Cleaning and recleaning the concentrate was tried to determine whether this would improve the grade of the final product. The sulphur assay was not raised appreciably by the use of a recleaner cell, so

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(12) Gisler, H. J., Factors Affecting Flotation, Deco Trefoil, Vol. 15, Aug. 1951.

it is doubtful that its use would be advisable in a minimum cost installation.

Twenty four complete flotation tests, with chemical analyses of all products and screen analyses of the head samples were made. Summaries of each test are given on the following pages, although a complete report is shown only for one typical test. Conclusions drawn from the test results will be found on the page following the data sheets.

#### FLOTATION TEST DATA

The following tests were made after the previously described preliminary tests, which determined pulp density and flotation time. In the description of these tests, the following factors will be constant, unless otherwise stated.

Time to make rougher concentrate--8 minutes

Time to make cleaner concentrate--2 minutes

Per cent solids in head feed--23 approximately  
pH--8.3

Conditioning time, promoter--3 minutes

Conditioning time, frother--1 minute

Only the sulphur present as iron sulphide is considered in the calculations because sulphates or sulphur present in zinc sulphide will not be useful in

the formation of sulphur dioxide in the roasting process. Complete assays were made to determine the exact composition of each product.

Flotation tests 1 to 7--Selection of promoter. This first series of tests was made for the purpose of selecting the most effective promoter. Each test was run under identical conditions of pulp density, pH, and time as explained above. The frother used was 0.1 pound of pine oil per ton of feed, conditioned for one minute. The promoting agents used were the xanthates; potassium isopropyl, potassium butyl, and sodium ethyl. Two tests were made with each of these reagents to eliminate the possibility of error. No visible differences could be noted in the process, but the chemical analyses showed that the highest grade of sulphur concentrate was produced when using isopropyl xanthate; and the highest recoveries were obtained when using isopropyl and butyl xanthates. The reagents were added as a 10 per cent solution, 0.2 pound per ton, and conditioned for 3 minutes. In tests 6 and 7, .15 pound per ton was used with equally good results.

Flotation tests 8 to 10--Selection of frother. Making use of the previously determined standards and the isopropyl xanthate promoter from the first series, this set of tests was made by varying the frothers. Pine oil had been used with good effect in the previous test,

providing a fairly tough and persistent froth with the desired finely divided air bubbles which gave good grade and recovery. One tenth of a pound of pine oil per ton added at the exit conditioner, with no further additions in any cells, was used. Cresylic acid used in the same manner was almost equally effective but gave a froth that was more brittle and the recovery was slightly lower. The higher alcohol frothers were tested in the form of Frother No. 52, which did not meet the standards set by the others. The froth did not have the carrying power or persistence needed. No additional tests were made as pine oil is very cheap and effective; or cresylic acid which is also cheap, could be used if the operator preferred it.

Flotation tests 11 to 13--Selection of pH. The pH of the feed was varied by the addition of sulphuric acid. The average pH of the zinc tailings used in these tests was 8.3, and it was thought that reduction of the alkalinity might improve the results. However, the addition of sufficient sulphuric acid to keep the pH at 7.8 and 7.0 throughout the circuit did not improve the results.

Flotation tests 14 to 19--Effect of particle size. The product of the grinding circuit showed considerable size variation, being coarser on some days than on others. Samples of the zinc tailings were taken at different

times and screen analyses of these tailings, which are the head feed to the iron circuit, were made. Then flotation tests were performed to determine the effect of fineness of grind upon grade of the final concentrate and recovery. The results of these tests are shown graphically on pages 36 and 37.

Flotation and filtration tests 20 to 24--Depressants.

Although good results had been obtained, it was decided to make some additional tests to determine the effect of carbonaceous depressants upon grade of the concentrate, recovery, and moisture content of the filter cake. It was hoped that a cleaner concentrate, which would have a lower moisture content after filtration, would result. Reagents 610 and 645 were used in the amount of 0.4 pound per ton, adding half in the conditioner and half in the cleaner cell. The resulting concentrates may be slightly higher in grade, but the recovery is somewhat lower. Filtration tests performed on the concentrates did not show appreciable improvement in the filtering characteristics.

Test No.	Frother	Promoter	pH	% S Conc.	% S Tails	Recovery	Misc.
1	pine oil	Z-4.	8.3	40.3	3.3	78.1	
2	" "	Z-4	8.3	39.8	3.2	76.9	
3	" "	Z-8	8.3	40.9	2.4	86.3	
4	" "	Z-8	8.3	41.3	2.2	88.2	
5	" "	Z-9	8.3	47.5	2.35	87.5	.2 lb. Z-9/Ton
6	" "	Z-9	8.3	46.1	2.2	88.3	.15 lb. Z-9/Ton
7	" "	Z-9	8.3	47.0	1.8	90.2	.15 lb. Z-9/Ton
8	Fr. # 52	Z-9	8.3	40.1	3.8	74.6	
9	Cresylic Acid	Z-9	8.3	46.8	2.3	87.4	
10	"	Z-9	8.3	47.1	2.4	86.6	
11	pine oil	Z-9	7.0	46.2	2.2	88.1	
12	" "	Z-9	7.8	47.1	2.1	87.8	
13	" "	Z-9	7.8	47.0	2.1	88.4	

TABLE II  
Flotation Test Data

Test No.	Frother	Promoter	pH	% S Conc.	% S Tails	Recovery	Misc.
14	pine oil	Z-9	8.3	46.1	2.2	89.2	screen analyses made of heads to FeS <sub>2</sub> circuit
15	" "	"	"	47.0	1.04	92.3	
16	" "	"	"	47.6	2.3	87.0	
17	" "	"	"	47.9	1.15	91.2	
18	" "	"	"	48.5	1.05	93.2	
19	" "	"	"	46.8	1.2	89.8	
20	" "	"	"	47.3	1.30	88.2	0.2 lb Reagent 610
21	" "	"	"	47.0	1.45	87.1	0.4 lb Reagent 610
22	" "	"	"	46.9	1.5	86.7	0.4 lb Reagent 610
23	" "	"	"	47.5	1.35	88.4	0.4 lb Reagent 645
24	" "	"	"	47.9	1.4	88.1	0.4 lb Reagent 645

TABLE III  
Flotation Test Data



Date of test Apr. 27, 1951Flotation test no. 15

Product	Weight	% weight	Assay		% of total		Other
			Iron as FeS <sub>2</sub>	Sulphur as FeS <sub>2</sub>	Iron as FeS <sub>2</sub>	Sulphur as FeS <sub>2</sub>	
Cleaner concentrate	99	10.54	40.90	47.0	51.7	50.5	Zn 0.75% Pb 0.0 %
Cleaner tails	156	16.6	21.50	24.7	40.4	41.8	
Rougher tails	685	72.9	0.9	1.04	7.9	7.7	oxide Fe = 1.3% total Fe = 2.2%
Head (composite)	940	100.04	8.33	9.85	100.0	100.0	oxide Fe = 1.10% total Fe = 9.33%

Only sulphur in the form of iron sulphide is considered in the assay and per cent of total columns.

Total iron equals iron as FeS<sub>2</sub> - iron in oxide form.

<u>Reagents used</u>	<u>Point of addition</u>	<u>Time</u>	<u>Amount</u>
Isopropyl xanthate	Conditioner	3 minutes	.15 lb./ton
Pine oil	Exit conditioner	1 minute	.1 lb./ton

TABLE IV

Typical Test Results Using Recommended Procedure

## CONCLUSIONS FROM FLOTATION TESTS

As a result of these flotation tests it is apparent that it is possible to make a high grade commercial concentrate, averaging at least 46 per cent sulphur; and to secure 90 per cent recovery, or better, in the flotation process. A summary of the factors entering into the process is given below.

**Time:** The best time for making the rougher concentrate was eight minutes. Although good recovery could be made in 6 to 7 minutes, the additional time is allowed as a factor of safety to take care of an increase in mine production and possible changes in the flotability of the ore. Two minutes of cleaning time gave adequate recovery and satisfactory grade of concentrate.

**Number of stages of flotation:** A rougher stage and a single cleaner for the rougher concentrate proved adequate. A recleaner circuit could be used but as a concentrate of satisfactory grade can be produced with a single cleaning, the additional expense probably is not warranted.

**pH:** A pH of 8.3 gave results equal to any, and should be used as it is the same as that of the tailings leaving the zinc circuit and eliminates the need of an additional reagent.

**Promoter:** Isopropyl xanthate and butyl xanthate both proved effective. The latter has greater promoter strength than the former which might make it more satisfactory for some ores. The isopropyl xanthate had adequate promoter effect for the Vinegar Hill ores and gave superior recovery, but later tests run on Calumet and Hecla zinc tailings indicated that the butyl xanthate was more effective on their ore. They are used in water solution in concentrations varying from 5 to 10 per cent. In the flotation tests .15 pounds per ton of feed was adequate. Best results were obtained by adding it in the conditioner and agitating for three minutes.

**Frother:** Pine oil gave satisfactory results at the lowest cost. The amount used was 0.1 pound per ton of feed with a conditioning time of one minute. No additional frother was needed in the cleaning circuit. Cresylic acid also gave fairly good results.

**Depressants:** The tests on the carbonaceous matter depressants added in varying quantities and at different points in the process failed to show appreciable improvement in either grade or recovery.

**Pulp density:** 20 to 25 per cent solids in the flotation

feed proved best in the iron circuit. This is the same as the tailings leaving the zinc circuit and consequently eliminates the need of a thickener, and will prove more satisfactory than a lower pulp density. Approximately 5 per cent solids in the cleaning cells was used.

Grind: The feed should be as coarse as possible. Of course, the size of grind must be dependent upon the grinding of the lead and zinc factions which are the primary elements sought in the mining and milling process. However, galena and sphalerite float readily when coarsely ground, provided that they are properly unlocked; thus by keeping the particle sizes as large as will give the best performance in the lead and zinc recovery circuits, the best recovery can be obtained in the iron circuit. The effect of particle sizes on grade of the marcasite concentrate and percentage recovery is shown by graphs on the following pages. This seems to be the key to the recovery problem and elimination of over-grinding should not prove difficult.

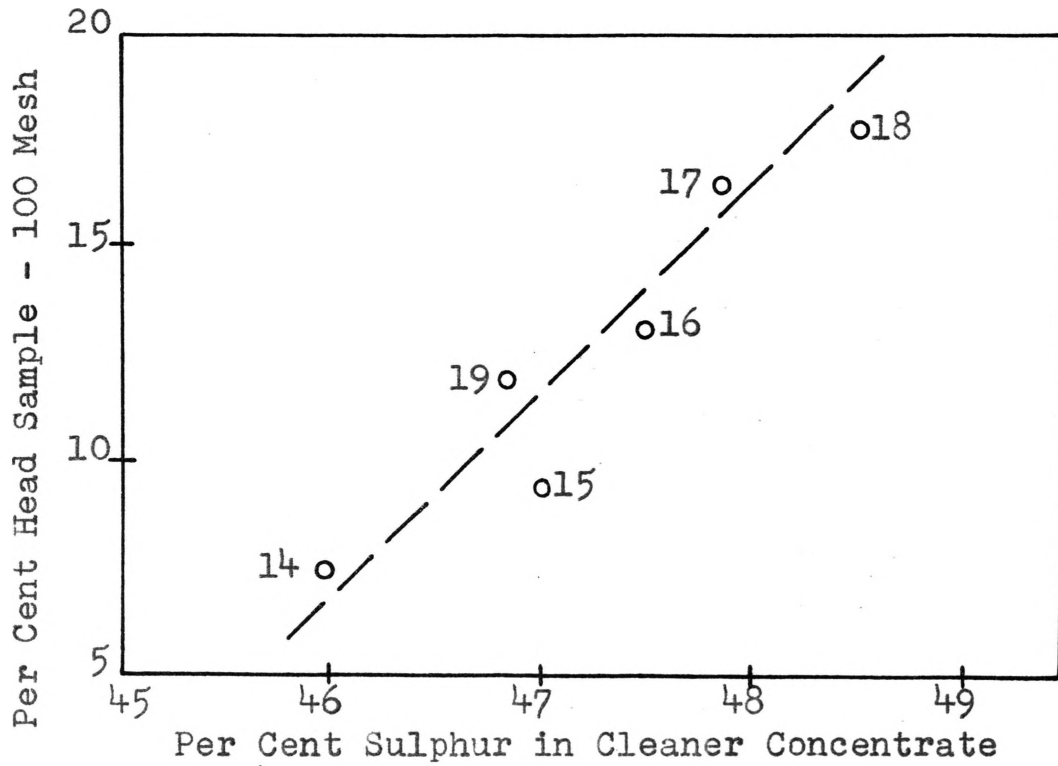


Figure 2. Graphical relationship between grade of  $\text{FeS}_2$  concentrate and per cent of heads retained on a 100 mesh screen.

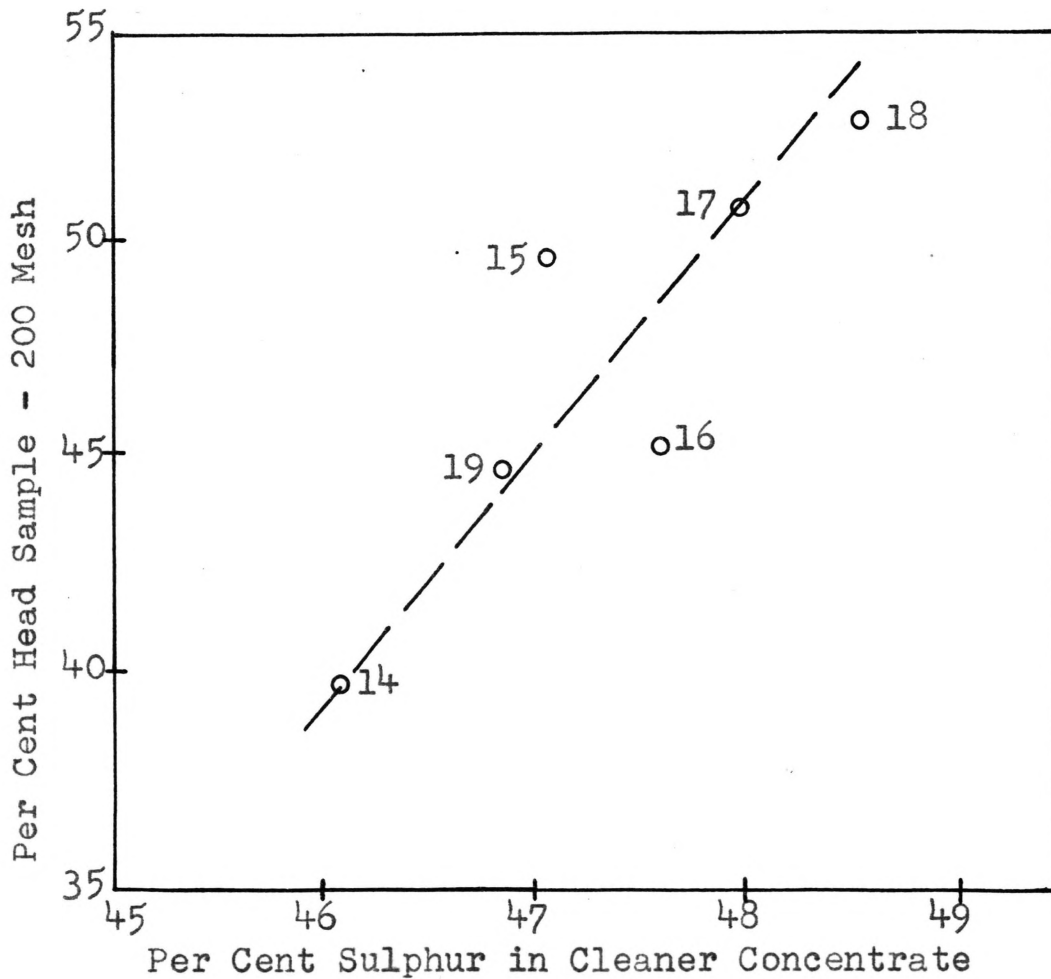


Figure 3. Graphical relationship between grade of  $\text{FeS}_2$  concentrate and per cent of heads retained on a 200 mesh screen.

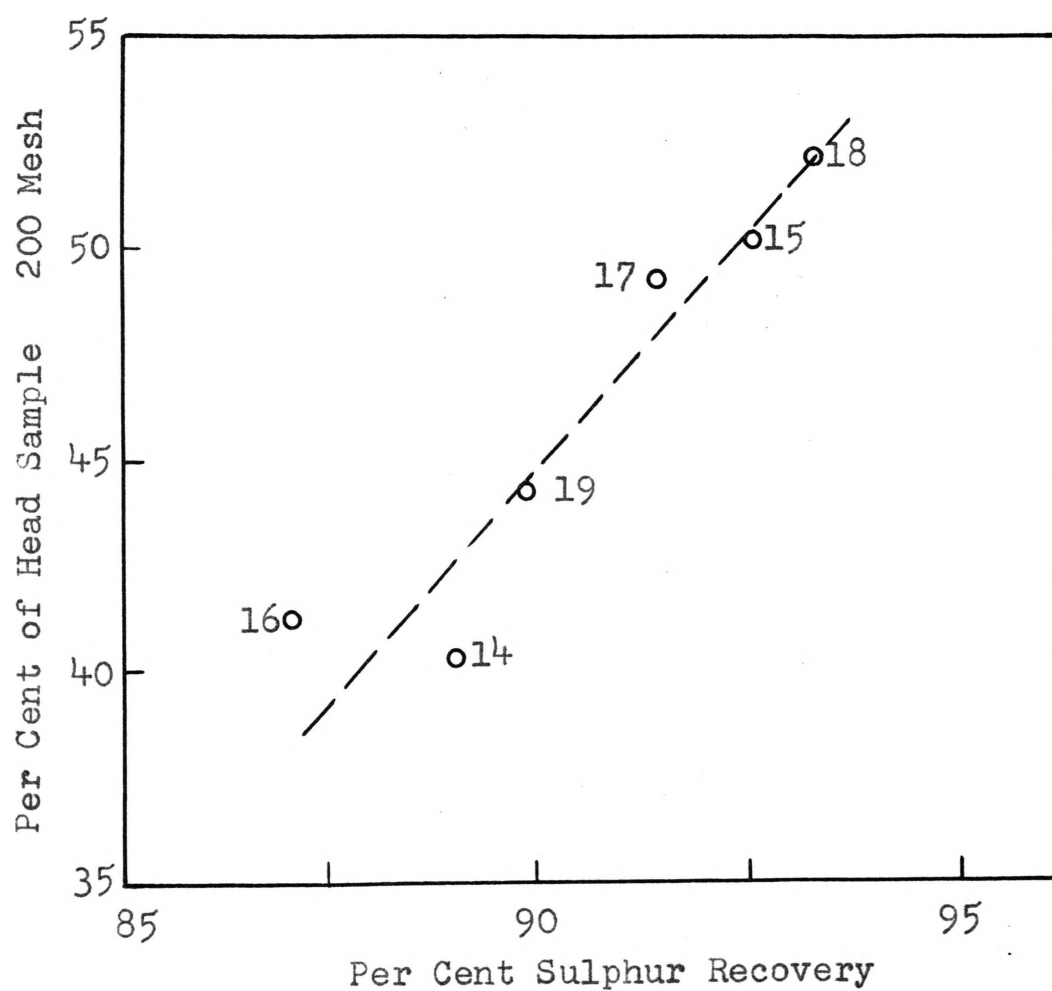


Figure 4. Graph of relationship between sulphur recovery and per cent of sample retained on a 200 mesh screen.

## CALCULATIONS FOR EQUIPMENT NEEDED

The equipment calculations and the costs that follow are based on the production and present milling procedure of the Vinegar Hill Zinc Company's mine and mill near Shullsburg, Wisconsin. The problem would be similar for any other mining company in the district as the ore and milling processes are similar; the tonnage being the only major variable. The Vinegar Hill mill daily treats 600 dry tons of mine run ore, averaging 5.5 per cent Fe. The jig mill has a ratio of concentration of 3 to 1 leaving 200 tons of flotation feed. After the lead and zinc circuits approximately 170 tons of zinc tailings are left as feed for the iron flotation.

Denver "Sub A" flotation cells are used in the mills of this district, so probably they will be used for additional circuits installed for marcasite recovery. Calculations will be based upon this type of equipment; however, the other types of flotation equipment should give equally good results.

The total volume of a ton of dry solids with a specific gravity of 3.3 in a pulp containing 23 per cent solids:

1 ton water = 32 cu. ft.

1 ton solids of 3.3 sp. gr. =  $\frac{32}{3.3} = 9.7$  cu. ft.

Ratio of solids to solution = 1 : 3.35

Total volume =  $9.7 + (3.35 \times 32) = 117$  cu. ft. of pulp

Volume of pulp per 24 hours =  $170 \times 117 = 19,900$  cu.ft.

$\frac{\text{Total cell capacity} \times (24 \times 60 \text{ min.})}{\text{Cu. ft. of pulp}} = \text{treatment time}$

$\frac{\text{Capacity} \times 1440 \text{ min}}{19,900} = 8 \text{ min.}$

Capacity of flotation cells = 110 cu. ft.

Thus, for the rougher circuit, a total capacity of 110 cubic feet is needed to give an 8 minute treatment time to the Vinegar Hill zinc tailings. This could be provided with 5-no. 18 Special Denver Sub A cells each of which has a capacity of 24 cubic feet. Any similar type of equipment providing this same capacity could be used. If the no. 18 Special flotation machines are used, one additional cell should be used for a cleaner. This will make a convenient 6 cell circuit.

Approximate cost of a 6 cell, no. 18 Special Sub A Flotation Machine, complete, with motors, mountings, switches, etc.--\$4300.

The pulp must be conditioned for three minutes so a conditioner must be supplied.

Conditioner capacity = daily pulp volume x treatment time  $\div (24 \times 60)$  minutes.

Conditioner capacity =  $\frac{19,900 \times 3}{24 \times 60} = 41.5$  cu. ft.

This volume can be provided with a 5' x 5' tank which has an available capacity of 64.5 cubic feet. This is the nearest larger size and will provide some



reserve for possible changes in tonnage or treatment time.

Approximate cost of a 5 ft. diam. x 5 ft. deep conditioner and agitator, complete, with motors, switch, etc.--\$750.

The flotation concentrate will have excess moisture removed by a disc filter. Filtration tests were made on laboratory filters to determine the characteristics of the concentrate. A thin filter cake is necessary because the iron sulphide is extremely fine. A 6 foot, 3 disc filter has a filter area of 144 sq. ft. which will bring the moisture content to approximately 10 per cent.

Approximate cost of a 6 foot diameter, 3 disc filter, complete, with all necessary vacuum equipment, motors, switches, etc.--\$5300.

The only additional equipment needed will be reagent feeders and a sand pump to pump the concentrate to the filter.

Approximate cost of two wet reagent feeders, complete, with motors and switches--\$300.

Approximate cost of one 2 inch centrifugal sand pump, complete, with motor and switch--\$425.

Equipment and installation costs are summarized in Table V.

Item	Material	Labor	Total
1 -- 5' x 5' conditioner	\$ 750	\$ 100	\$ 850
1 -- 6 cell # 18 Sp. flotation machine or equivalent	4300	400	4700
1 -- 2" centrifugal sand pump	425	100	525
1 -- 6' , 3 disc filter	5300	300	5600
2 -- wet, reagent feeders	300	100	400
Piping and electrical work	200	800	1000
Conveyor, filter to storage	800	200	1000
Building addition (filter and storage)	3000	3100	6100
	<u>\$15,075</u>	<u>\$5100</u>	<u>\$20,175</u>

These estimates are based upon the Vinegar Hill Zinc Company's production of 600 tons of mine-run ore per day.

TABLE V

Estimated Equipment and Installation Expense for Iron Sulphide Concentration

TABLE VI

## Production Calculations Based Upon Recovery Tests

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Calculations based on 600 dry tons per day and 5.50 per cent Fe (average of Fe assay of crude mine ore treated in Vinegar Hill jig mill April-May, 1951)

Assume 75 per cent recovery Fe in jig mill (from plant tests)--One ton feed-2000 pounds x .0550 x .75 = 82.5 pounds Fe per ton to float mill feed.

Assume 90 per cent recovery Fe in Pb and Zn Float Circuits-  
 $82.5 \times 90 = 74.25$  pounds Fe in float zinc tails

From W.I.T. Laboratory Tests deduct 15 per cent as Fe oxide-- $.85 \times 74.25 = 63.11$  pounds Fe

Assume 75 per cent recovery Fe in iron flotation and filtering-- $.75 \times 63.11 = 47.33$  pounds Fe recovered per ton of feed

Assume grade of 40 per cent Fe in  $\text{FeS}_2$  concentrates produced in Fe flotation

$\frac{47.33}{.40} = 118.33$  pounds of 40 per cent Fe concentrates per ton of feed

$\frac{118.33}{2000} = 0.05917$  tons of 40 per cent Fe concentrates (containing 46 per cent sulphur) per ton of mine ore

$0.05917 \times 46 \text{ units} = 2.722 \text{ units Sulphur/ton of mine ore}$

Tons of 46 per cent Sulphur concentrates produced per day-- $600 \text{ tons} \times .05917 = 35.5 \text{ tons}$

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TABLE VII

## Cost Estimates of Fe Flotation Per Ton Crude Mine Ore

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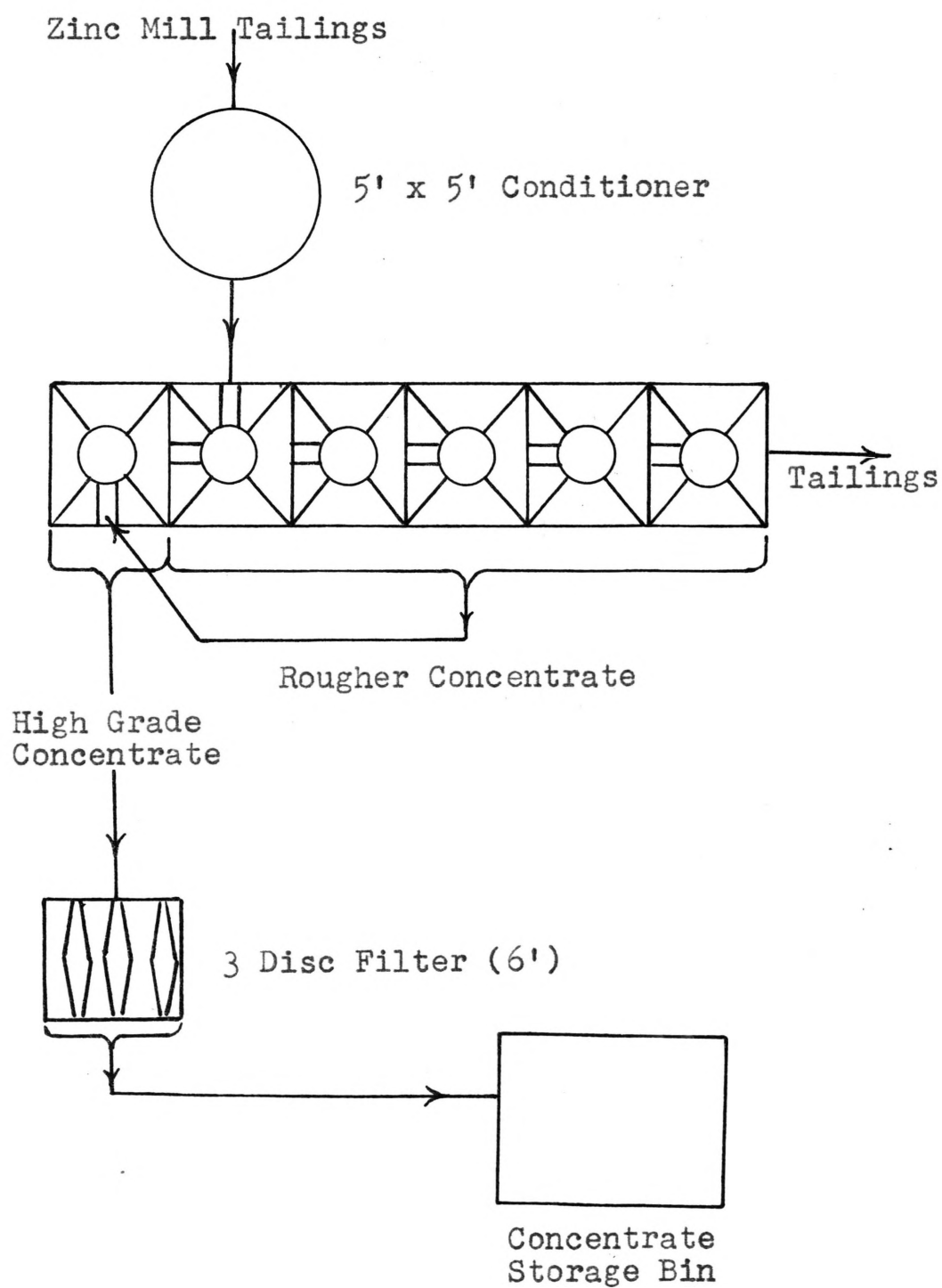
Labor - (3 men, 48 hours at \$1.10)	\$0.047
Power - 50 HP	0.024
Reagents - 4 cents per ton float feed	0.011
Repairs and supplies	0.030
<hr/>	
Total cost less overhead, amortization, and interest (per ton crude mine ore)	\$0.112

One ton of 46 per cent  $\text{FeS}_2$  concentrate will be produced from 17 tons of average crude mine ore. Thus:

Milling cost per ton of concentrate = \$1.90

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Figure 5

Flowsheet for Iron Sulphide Concentration

## Financial Value of the Project

The 1951 price of brimstone was \$22.00 per gross ton f.o.b. Gulf Coast ports. The shipping cost to Dubuque, Iowa (which is the nearest location of a chemical plant interested in purchasing iron sulphide) is approximately \$4.00 per gross ton by barge, and \$5.50 by rail; making the total cost \$26.00 to \$27.50 per gross ton of sulphur. The paper companies in northern Wisconsin pay about \$30 per ton delivered price. To determine the approximate value of iron sulphide as a source of sulphur, these figures may be converted to short ton values, as the 2000 pound ton is the standard used in this district for all purposes. Thus, the value of a short ton of sulphur received in Dubuque by rail would be \$24.50, or  $24\frac{1}{2}$  cents per short ton unit. The paper companies pay 28 cents per short ton unit.

It is believed that the price of brimstone will be substantially increased; and this price increase in addition to the decreasing availability will cause more interest in the use of iron sulphide concentrates as a source of sulphur. At the present time, iron sulphide concentrates can be sold for 16 cents per unit of sulphur content delivered in the Chicago district. This price is not sufficiently high to interest the mine operators, for after deducting rail and trucking costs there would be insufficient money left to pay operating

costs and a reasonable profit. However, chemical and paper company officials have indicated willingness to pay an amount more nearly equal to the cost of brimstone in order to assure themselves of a continuing supply of sulphur. A reasonable price to be expected would be 20 cents per short ton unit of sulphur content delivered within the surrounding market area, or 16 cents per short ton unit f.o.b. mine. (20 cents per short ton unit = 22.4 cents per long ton unit.) If this figure were guaranteed with a contract running for a period of time sufficiently long to assure recovery of the investment in buildings and equipment, the mine operators would be willing to undertake the project.

Assuming a price of 20 cents per short ton unit of sulphur content, the following calculations show the value of the iron sulphide to the Vinegar Hill Zinc Company.

One ton of 46 per cent sulphur concentrate	\$9.20
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Transportation to Dubuque, Iowa (by truck, 30 miles at 8 cents per ton mile. Cost per ton of dry FeS <sub>2</sub> concentrate, assuming 10 per cent moisture).	\$2.67
--	--------

Milling costs	\$1.90	\$4.57
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Net value per ton of 46 per cent sulphur concentrate, omitting amortization		<hr/> \$4.63
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Value of daily production of 35.5 tons	\$165.00
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Annual value of FeS <sub>2</sub> , 300 day year, total production 10,650 tons	\$49,500.00
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Thus it may be seen that this type of operation could be quite profitable to the mine owners as well as an aid in alleviating a serious shortage of a critical material. The one company used as an example would make a net profit (except for amortization and interest) of approximately \$50,000 per year. From the cost sheet for this company on page 40, the estimated cost of equipment, building, and installation is found to be about \$20,000. As the entire first cost of the operation can be paid off in the first year, in addition to a nice return on the investment; this should prove attractive to the mine owner



TABLE VIII

## Daily Tonnage of Crude Ore from Wisconsin-Illinois Mines

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	Present	Proposed Increase
Calumet and Hecla	1200	
Eagle-Picher	1200	
Vinegar Hill Zinc Company	600	150
Tri-State Mining Company	600	
Mifflin Mining Company	120	180
Dodgeville Mining Company		200
Cuba Mining Company (included with Vinegar Hill)		
Little Grant Mine		200
George M. Baker	200	
Parish	200	
New Jersey Zinc Company		?*
Enterprise		?*
	<hr/>	<hr/>
	4120	

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\* Not yet producing ore

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## District Potentials

The Upper Mississippi Valley Zinc District is regaining importance as a major producing region. Several of the country's largest mining companies are now operating in the district and another is conducting an extensive exploration program. An excellent future for the district seems to be assured as the mining companies are opening new ore bodies; and the United States Geological Survey has revealed the presence of sufficient ore reserves to last for many years. The U.S.G.S. has been active in the Illinois and Wisconsin sections of the district for the past ten years and are now conducting an extensive exploration program on the Iowa side of the Mississippi River. The latter area has been almost completely inactive since the early "lead digging" days, but old records and present drilling tends to indicate that important ore bodies are to be found there.

In past years most of the mining operations have been small and short lived. In contrast with these, the mining companies now active in the district are operations designed for large production and long life, with large ore bodies thoroughly proved by careful exploration programs to assure sufficient reserves for many years of operation.

The daily production of the district is now over 4000 tons of crude ore, and with the expansion programs of the active mining companies and activation of new ones the production should increase to approximately 5000 tons per day before the end of 1952.

The iron sulphide content of these ores will average at least as high as the  $\text{FeS}_2$  content of the Vinegar Hill Zinc Company ore which was used as the basis for the tests and calculations of this report. Assuming the same sulphur assay, the present crude ore production of 4,120 tons per day, and the same recovery in the milling process, the potential production of 46 per cent sulphur concentrate would be:

$$\frac{35.5}{600} \times 4120 = 244 \text{ tons of 46 per cent } \text{FeS}_2 \text{ concentrate}$$

$$244 \text{ tons} \times .46 = 112 \text{ tons of sulphur content}$$

$$112 \times 300 = 33,600 \text{ tons of sulphur annually}$$

$$33,600 \times \$20 = \$672,000 \text{ annual value of iron sulphide concentrate at 20 cents per short ton unit of sulphur.}$$

The daily production of 244 tons of iron sulphide concentrate containing 46 per cent sulphur could be increased by 15 to 20 per cent within a short time due to the steadily increasing production of ore as a source of zinc and lead.

### By-Product Possibilities

The roasting of iron sulphide would result in the production of the desired sulphur dioxide gas and would leave a residue consisting largely of iron oxide. In the 73,000 tons of iron sulphide concentrate which could be produced annually, there would be 29,200 tons of iron.

Mr. R. Wynkoop, Technical Director of the Algonquin Chemical Company estimates that the roasting of the flotation concentrate might produce the following calcine:  
(13)

$\text{Fe}_2 \text{O}_3$	85.3
$\text{Zn SO}_4$	3.7
$\text{Ca O}$	11.0
	<hr/>
	100.0

This calcine would assay 60 per cent Fe and the roasting of 73,000 tons of iron sulphide concentrate would result in the production of 48,500 tons of iron oxide concentrate containing 60 per cent iron. This material could possibly be marketed as a blast furnace charge if the difficulty of its fineness can be overcome. It might also be used as a paint pigment, in foundry work, or for other uses to which red iron oxide is put

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(13) Wynkoop, R., Personal Communication, Aug. 8, 1951.

in the chemical and other industries. This presents another attractive feature in the use of iron sulphides, as a market for the iron oxide would be of considerable financial importance.

## CONCLUSION

By making use of the iron sulphides of the Upper Mississippi Valley zinc district, the sulphur consuming industries of the area can assure themselves of a supply of that element that will satisfy most of their needs. Over 33,000 tons of sulphur (in the form of iron sulphide concentrates) could be made available annually by the mining companies of this district; and undoubtedly this figure could eventually be increased to 50,000 tons of sulphur equivalent annually.

The sulphur shortage at this time is not enough to have caused serious production cutbacks. However, the stockpiles of brimstone have dwindled to the danger point, and the officials of brimstone producing companies state that they cannot produce enough to take care of the steadily increasing demand. To prevent the harmful effect on industry of a shortage of this essential element, other sources must be found. Sulphur in the form of brimstone has been very cheap and is the most easily and conveniently used form of the element for making all of the useful sulphur compounds. A large percentage of it is burned to form sulphur dioxide or sulphuric acid, and for this purpose iron sulphide is equally useful. The disadvantage in the use of iron sulphide is that the plant necessary to burn it, and its operation, is considerably more expensive than that

for burning brimstone. These arguments made brimstone the more ready choice when it was cheap and readily available; now, however, it is in short supply and a considerable price increase is anticipated, thus the use of iron sulphide as a substitute can be given serious consideration. The new low cost FluoSolids process for burning iron sulphide presents an ideal process for handling the marcasite concentrates produced in this district, and could be installed at paper mills or other points of use of sulphur gases. This equipment helps to eliminate one objection to the use of iron sulphides. The other big arguments in favor of brimstone were (1) low cost, and (2) availability. The latter argument can now be eliminated, so let us consider the factor of cost. Consumers of brimstone in this area must pay approximately  $24\frac{1}{2}$  to 28 cents per short ton unit of sulphur (delivered price), and this figure is expected to rise considerably higher. Iron sulphide concentrate could be purchased at 20 cents per long ton unit of sulphur (delivered price). This means that the unit cost of sulphur in the form of iron sulphide would be 19 to 29 per cent less than in the form of brimstone. This price differential should take care of the additional processing cost involved in its use.

No positive action has been taken by interested

parties at this time, but chemical and paper companies have exhibited great interest in the results of these investigations and desire to assure themselves of a continuing supply of sulphur, and this district promises a nearby practical source. The mining companies have not attempted to recover the marcasite because they will not make the considerable expenditure necessary without a definite promise of a satisfactory price (above the present 16 cents per long ton unit now offered) and a continuous market for their output. An agreement could be made between the mine operators and the consumers which would be mutually profitable. The iron sulphide is going into tailings piles from which it cannot be recovered--a total loss to both parties.



### SUMMARY

The factors favoring the use of iron sulphides as a source of sulphur, may be briefly summarized by the following statements:

- 1) Production of brimstone cannot meet the industrial demand for sulphur, as a result industry faces production cutbacks.
- 2) A high grade commercial iron sulphide concentrate can be produced from zinc ores of this district.
- 3) Large ore reserves give promise of a continuous supply of sulphur in this form.
- 4) The Dorr Company's FluoSolids process for roasting sulphides provides a very satisfactory method for utilizing the sulphur in this form.
- 5) Iron sulphide concentrates would provide sulphur at a lower unit cost than brimstone.

The marcasite which is now considered a waste product can be recovered from the zinc tailings of the present milling practice by the flotation process. By floating this material, over 90 per cent of the iron sulphide present in the zinc tailings will be found in the concentrate produced by the cleaner cells, and this concentrate will assay 46 per cent sulphur, or higher. As a conservative estimate, the mills of southwestern Wisconsin and northern Illinois could produce annually the

equivalent of 33,600 tons of sulphur. The concentration process described in this paper is simple and of low cost.

A decision to use this material as a source of sulphur would be beneficial to the mining companies, the mining district, the sulphur consuming companies, and the entire country. If the mining companies could save their  $\text{FeS}_2$  as shown in this report and sell it at the compromise price of 20 cents per unit, they would receive \$672,000 based upon present crude ore production. This would give a high rate of return on the investment required, and would aid the district's prosperity. The chemical and paper companies would have a satisfactory supply of sulphur, and the entire country would benefit by the release of the equivalent amount of brimstone for other essential purposes.

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